

PREPARATION AND UTILIZATION OF HIGHLY TRANSPARENT AND VISCIOUS DISPERSION OF PHOSPHORYLATED CELLULOSE NANOFIBERS

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1 INTRODUCTION

Increased environmental awareness has highlighted bio-based fiber materials as substitutes to fossil-based material since they are made from renewable resources. Recently, cellulose nanofibers (CNFs) have attracted attention as a new promising bio-based nanomaterial because of their excellent properties such as high tensile strength [1], high crystal modulus [2] and low coefficient of linear thermal expansion (CLTE) [3].

Chemical pre-treatment such as TEMPO oxidation [4], carboxymethylation [5], [6], esterification with maleic anhydride [7], and cationization [8] is preferred over mechanical treatment for CNFs production since less energy is used.

In this work, we have recently found that CNFs with uniform widths of 3–4 nm can be obtained in approximately 100% gravimetric yield by high-pressure homogenization of a phosphorylated pulp slurry. In addition, the obtained phosphorylated CNF dispersion is highly transparent and viscous. Furthermore, it is shown that the properties of phosphorylated CNF film are unique compared with a glass substrates, as well as conventional plastic films.

2 METHODS

2.1 Phosphorylation

Softwood pulp sheets were soaked in an aqueous solution of urea and $\text{NH}_4\text{H}_2\text{PO}_4$. The treated pulp was dried and cured in hot air (165°C , 200 s) to introduce phosphate groups in the pulp. After that, phosphorylated pulp was washed with DI water repeatedly and neutralized with aqueous NaOH solution (Figure 1) [9].

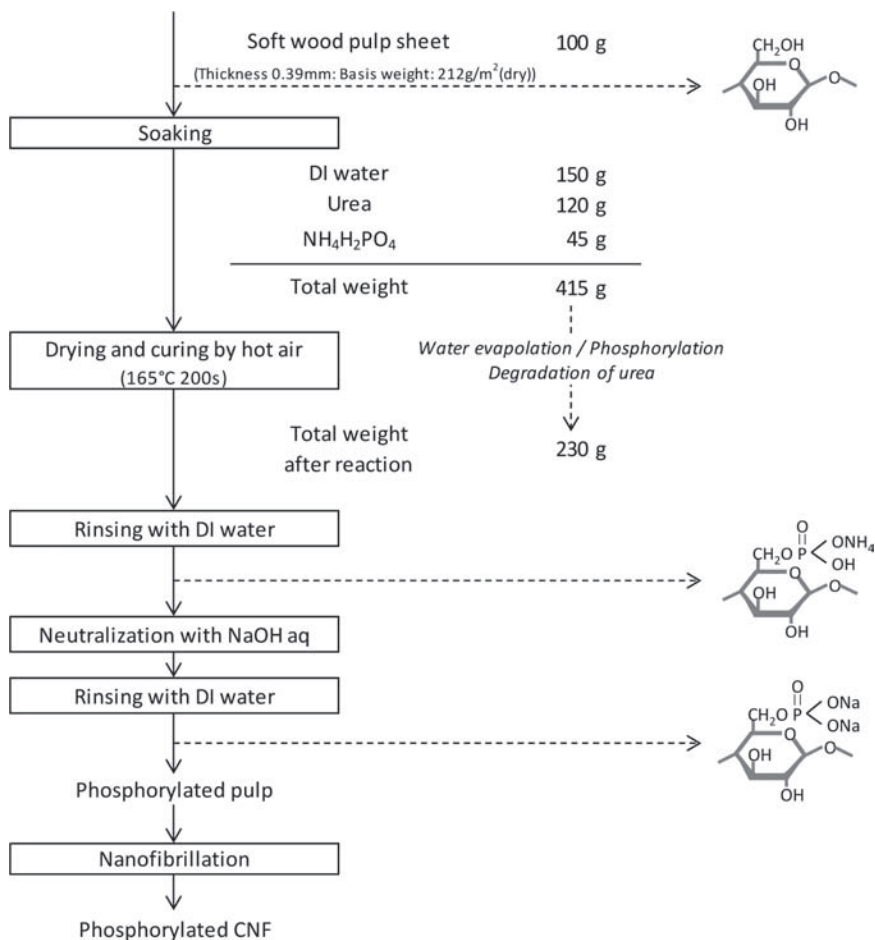


Figure 1. Preparation scheme of phosphorylated pulp and CNF.

2.2 Nanofibrillation

A 2 wt% phosphorylated pulp slurry was mechanically disintegrated using a high-pressure homogenizer at 200 MPa. The number of passes was 1 to 5.

2.3 Analyses

Material properties of the obtained phosphorylated pulp, phosphorylated CNF dispersion and phosphorylated CNF film were studied by: X-ray diffraction, viscosity-average degree of polymerization of the phosphorylated pulp, gravimetric yield, total light transmittance, viscosity, TEM imaging of phosphorylated CNF dispersion, similarly to [9].

Furthermore, optical and mechanical properties of the films were measured according to JIS K 7361, 7136 and 7127, respectively. The coefficient of linear thermal expansion (CLTE) was measured using a thermomechanical analyzer (TMA SS7100, Hitachi High-Technologies Corporation, Tokyo Japan). The range of temperature for calculation of CLTE was 60–100 °C.

3 RESULTS AND DISCUSSION

3.1 Phosphorylated pulp

The phosphorylated pulp morphology was the similar as the original pulp and no significant coloration could be observed. The amount of phosphorous in the phosphorylated pulp was 1.23 mmol/g. The crystal structure and crystallinity indices of the phosphorylated pulp and the original pulp were determined using X-ray diffractometry and solid-state ¹³C NMR (Figure 2, Figure 3 and Table 1). The cellulose I crystal structure did not change after phosphorylation, and the crystallinity index of the phosphorylated pulp, calculated by Segal's method, was equivalent to that of the original pulp (Table 1). These results indicate that the phosphate groups were introduced onto the cellulose microfibril surfaces without changing the crystal structure. In addition, viscosity-average degree of polymerization (DP_v) was also unchanged even after phosphorylation which conducted under acidic condition (Table 1).

3.2 Phosphorylated CNF dispersion

When the phosphorylated pulp slurry was homogenized at high pressure, gravimetric yield (Figure 4, *top-left*), transparency (Figure 4, *top-right*) and viscosity (Figure 4, *bottom*) increased sharply. The obtained dispersion after 5 passes of homogenization was gel-like without any additional treatment (condensation,

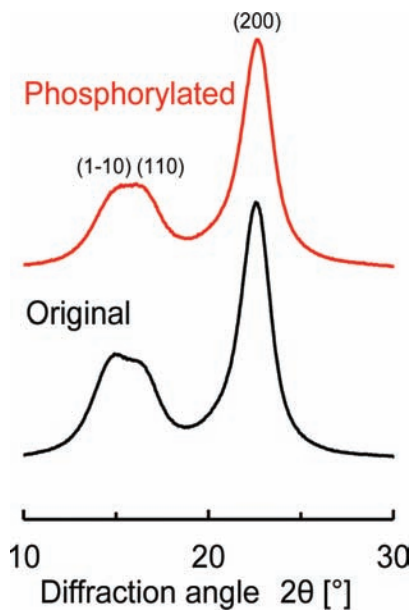


Figure 2. X-ray diffraction patterns of original pulp and phosphorylated pulp.

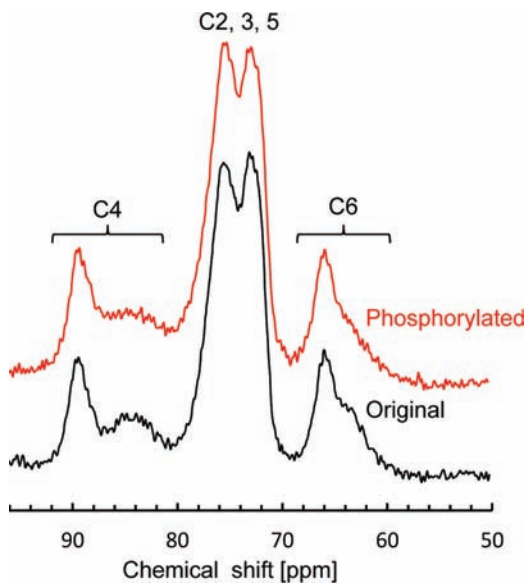


Figure 3. Solid-state ¹³C NMR spectra of original pulp and phosphorylated pulp.

Table 1. Crystal structures, crystallinity indices and DP_v of original pulp and phosphorylated pulp

Pulp	Crystal structure	Crystallinity index (%)	DP_v^\dagger
Original	Cellulose I	88.1	846
Phosphorylated	Cellulose I	87.5	855

† Viscosity-average degree of polymerization

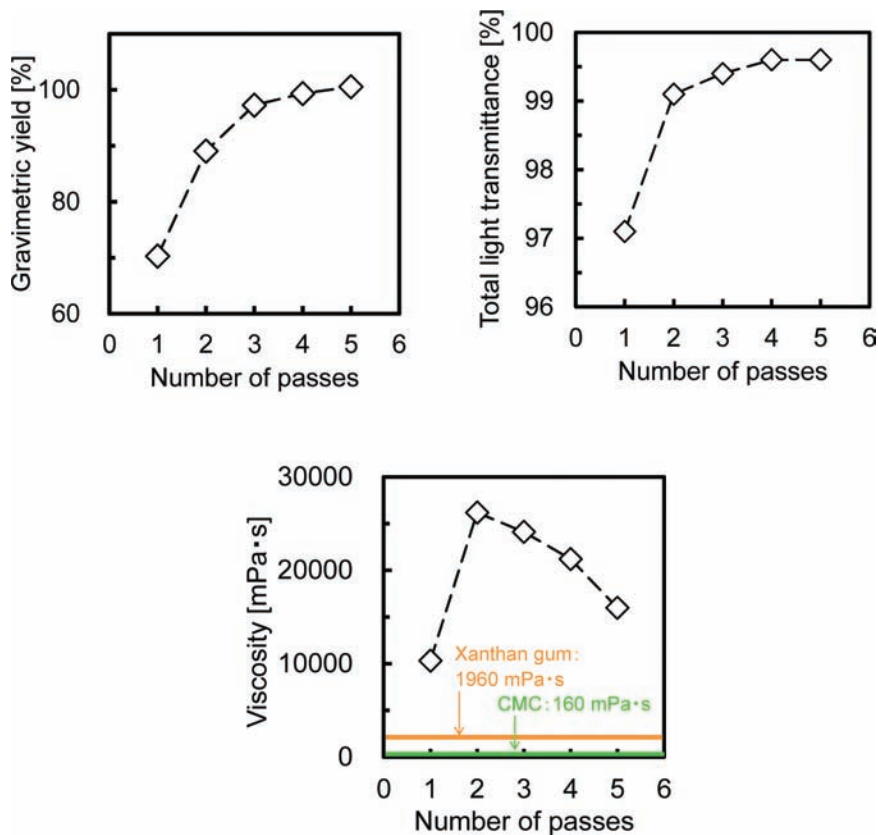
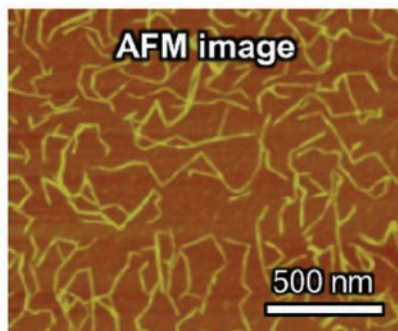


Figure 4. (Top-left) Gravimetric yields of phosphorylated CNF dispersions (0.1 wt%) as a function of a number of passes during high-pressure homogenization. (Top-right) Total light transmittance of phosphorylated CNF dispersions (0.2 wt%) as a function of the number of passes during high-pressure homogenization. (Bottom) Viscosity of phosphorylated CNF dispersions (0.4 wt%) and conventional thickeners as a function of the number of passes during high-pressure homogenization.

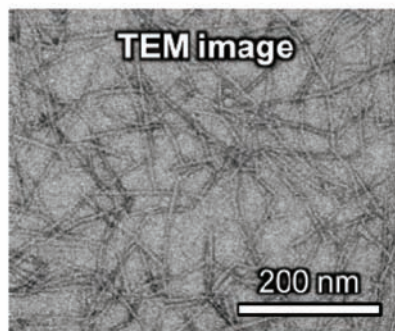
addition of metal cations or acids etc., Figure 5(a)). The presence of CNFs with widths of 3–4 nm was confirmed using AFM and TEM (Figure 5(b) and 5(c)). Moreover, the gravimetric yield (yield of individual CNFs), which can be calculated based on the ratio of the CNF concentration in the supernatant liquid after centrifugation (12,000 g) to a solid concentration before centrifugation, reached approximately 100% (Figure 4).



(a)



(b)



(c)

Figure 5. (a) Photograph of 2 wt% phosphorylated CNF dispersion; (b) AFM image of phosphorylated CNFs; and (c) TEM image of phosphorylated CNFs.

Due to fiber size and its dispersibility, the phosphorylated CNF dispersion was highly transparent and was highly viscous compared to that of other conventional thickeners (Figure 4, *top-right* and *bottom*). High viscosity also assumed to be resulted from high DP_v , which was unchanged during phosphorylation. By taking advantage of these features, the phosphorylated CNF dispersion can be used as a high performance thickener in many fields such as cosmetic, food and other industrial fields.

3.3 Phosphorylated CNF film

When the CNF dispersion was dried, the CNFs were densely packed together by capillary action during the evaporation of the water. In this way, continuous CNF film was obtained (Figure 6). Similar to the CNF dispersion, the CNF film had clear appearance and the surface of it was very smooth.

The CNF film has higher transmittance, higher Young's modulus, higher heat resistance, and lower coefficient of liner thermal expansion (CLTE) than conventional plastic films such as PET and PEN (Table 2, Table 3). Especially, CLTE



Figure 6. Photographs of continuous transparent CNF film.

of the CNF film (7.2 ppm/K) was as low as that of glass substrate (~3 ppm/K). Furthermore, the CNF film had tolerability to organic solvent (e.g. methanol, acetone, THF, toluene), and so high flexibility that we could wind it around 1mm diameter shaft. The CNF film is also foldable without whitening on bending.

The properties of the CNF film were so unique compared with a glass substrate, and conventional plastic films such as PET and PEN. These superior properties make this film useful as a material for flexible OLED display, foldable solar cell, and TFT substrate.

Table 2. Properties of transparent CNF film[†]

<i>Transmittance (%)</i>	<i>Haze (%)</i>	<i>Tensile strength (MPa)</i>	<i>Young's modulus (GPa)</i>
91.4	0.5	223	11.6
<i>CLTE^{††} (ppm/K)</i>	<i>T_g^{†††} (under 200 °C)</i>	<i>Decomposition temperature (°C)</i>	<i>Tolerant to organic solvent</i>
7.2	Nothing	312	Good

[†] Thickness: 25 μ m

^{††} CLTE: Coefficient of Liner Thermal Expansion

^{†††} T_g: Glass transition temperature

Table 3. Properties of conventional plastic films[†]

<i>Film</i>	<i>Transmittance (%)</i>	<i>Haze (%)</i>	<i>Tensile strength (MPa)</i>	<i>Young's modulus (GPa)</i>	<i>CLTE^{††} (ppm/K)</i>	<i>T_g^{†††} (°C)</i>
PET	87.0	0.5–1.5	120–170	3.2–4.2	70	70
PEN	87.0	–	550	12.2	18	155
TAC	92.5	0.5	77.6	4.5	32	40

[†] Thickness: 125 μ m (PET, PEN), 60 μ m (TAC)

^{††} CLTE: Coefficient of Liner Thermal Expansion

^{†††} T_g: Glass transition temperature

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Transcription of Discussion

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Jose Iribarne WestRock

Thank you very much. Very interesting. Can you comment on the mechanical energy that you still need to produce the phosphorylated CNF please?

Yuichi Noguchi Oji Holdings Corporation

I don't have the exact data on that, but it is reduced greatly because the phosphate group has two acidic groups in one substitution group and we can substitute 3 hydroxyl groups in two glucose units. Is this correct answer to your question?

Gil Garnier Monash University

Excellent presentation. Why are your gels so clear and so viscous?

Discussion

Yuichi Noguchi

That is because phosphorylated pulp has many acidic (ionic) groups. So that the repulsion power for fibrillation is strong.

Gil Garnier

Are you telling me that the diameter of your gel is smaller than what you achieve with TEMPO?

Yuichi Noguchi

I don't think so because microfibrils of wood pulp are the same, so it is just the difference of how to substitute hydroxyl groups.

Gil Garnier

This is physics. It is just matter of size and diffraction if you are smaller than the wavelength of light you are clear. If you are higher, you have some absorbance, therefore physics tells us that nothing prevents light transmittance, so can you discuss in terms of the fibres' length and diameter?

Yuichi Noguchi

Diameter?

Gil Garnier

Because you said that your diameter was 3–4 nanometers.

Yuichi Noguchi

Yes, yes.

Gil Garnier

With Professor Isogai with TEMPO, we saw that the diameter was constant at 3 nm. Because length would not affect it, it has to be the diameter, so therefore you must have to be smaller, or to have fewer bigger particles, but anyway, why is your gel so viscous?

Yuichi Noguchi

High viscosity is due to long length of cellulose nanofibres and also the hydration effect of phosphate groups. It means that water is not easily moved on cellulose microfibril surface, so it results in extremely high viscosity.

Gil Garnier

Could you explain that in terms of electrostatic interaction and entanglement of the fibre network or have you measured the fibre length distribution for your gel?

Yuichi Noguchi

Sorry, I have not measured the fibre length distribution.

Gil Garnier

And the last question is, you showed that the viscosity reaches maximum after two passes and then it decreases, why?

Yuichi Noguchi

I think the decrease is because of depolymerization via homogenization. The increase is due to nanofibrillation (increase of surface area and entanglement of the nanofibre). It seems that the effect of nanofibrillation was almost completed by 2 passes.

Harshad Pande Domtar Inc

Any comments on the dryness? How did you dry the CNF that made the film?

Yuichi Noguchi

It was dried to 95% solids or so.

Harshad Pande

Was it flash dried, freeze dried . . . ?

Discussion

Yuichi Noguchi

Sorry. It is a secret.

Jean-Claude Roux Grenoble University

On this slide, you can see that you use homogenizer and my question is what is the duration of your trial? Is it 200 seconds or is it different?

Yuichi Noguchi

It depends on the weight of pulp slurry. We control this.

Jean-Claude Roux

I am sure that you control this.

Yuichi Noguchi

I think the time for fibrillation is in the order of milliseconds, but we can't measure this exactly.

Jean-Claude Roux

So you cannot get me the answer.

Yuichi Noguchi

I am sorry.